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Reactions of Sulfenyl Chloride Derivatives of Metal β-Diketonates

I. V. Svistunova and N. P. Shapkin

Far Eastern Federal University, ul. Oktyabr'skaya 27, Vladivostok, 690950 Russia
e-mail: irasvist@gmail.com

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Abstract—The reactions of sulfenyl chloride derivatives of rhodium and ruthenium acetylacetonates as well as of chromium(III) and cobalt(III) β-diketonates (with β-phenyl groups) have been studied. The studied complexes can participate in the substitution and addition reactions. As compared with the previously studied sulfenyl chlorides of acetylacetonate complexes, many side processes occur in the case of β-phenyl chelates; they decrease the products yield and complicate their purification. In the case of dibenzoylmethenate complexes, reduction reactions can easily occur, giving the partially substituted chelates impurity.

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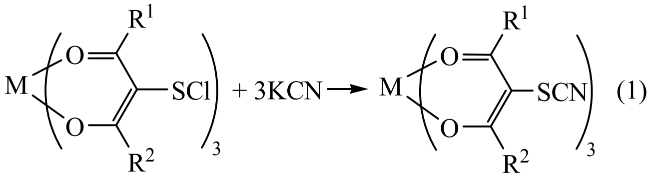
Until recently, a wide range of reactions of sulfenyl chlorides containing metal chelate fragments has been described [1–4]. However, these works has been carried out using sulfenyl chlorides of chromium, cobalt, and aluminum acetylacetonates, known since 1961 [5]. Recently, we have prepared and described new sulfenyl chloride derivatives of rhodium(III) and ruthenium(III) and the SCl-derivatives of metal chelates containing phenyl groups as β-substituents: sulfenyl chlorides of benzoylacetonate and dibenzoylmethenate complexes [6]. In this work we report the reactions of these new sulfenyl chloride derivatives of metal β-diketonates.

As a simplest example of substitution reaction involving SCl group, we studied the complexes interaction with potassium cyanide; thiocyanates were expected as its product, many of which were described in the literature.

The reaction was performed in the mixed solvent, acetic acid–THF. Using acetic acid alone (as suggested in [5]) was not convenient, as sulfenyl chloride derivatives of benzoylacetonate (bzac) and dibenzoylmethenate (dbm) complexes were insoluble in CH_3COOH. A model experiment with $Cr(acacSCl)_3$ revealed that in the mixed solvent the expected thiocyanate formation occurred rapidly, and high yield was achieved.

The reaction occurred most smoothly in the cases of $Cr(bzacSCl)_3$ (**I**) and $Rh(acacSCl)_3$ (**II**). In the interaction of those sulfenyl chlorides with potassium cyanide, the thiocyanates were obtained with the yield of 45 and 90%, respectively. The products **V** and **VI** were identified according to the reported melting points (Table 1). In the both cases, minor products were revealed by TLC, they were not studied.



I, II, III, IV **V, VI, VII, VIII**

M, R^1, R^2 = Cr, Ph, CH_3 (**I, V**); Rh, CH_3, CH_3 (**II, VI**); Cr, Ph, Ph (**III, VII**); Co, Ph, Ph (**IV, VIII**).

The interaction of SCl-substituted chromium dibenzoylmethenate with potassium cyanide gave two major products isolated by chromatography. The less mobile one was identified as tristhiocyanate **VII** (yield 48–50%). Its structure was confirmed by TLC [R_f identical to that of $Cr(dbmSCN)_3$ prepared from $Cr(dbmH)_3$ and $(SCN)_2$] as well as by melting point.

The more mobile product was identified as disubstituted thiocyanate $Cr(dbmH)(dbmSCN)_2$ (**IX**), its structure was confirmed by elemental analysis. Additionally, structure of **IX** was deduced from TLC by comparison with a mixture of partially substituted thiocyanates of chromium(III) dibenzoylmethenate.

Table 1. Yield and characteristics of compounds **V–XXVII**

Comp. no.	Compound	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
				C	P (Cl)	S		C	P (Cl)	S
V	$Cr(bzacSCN)_3$	45	170–173[a]			13.98	$C_{33}H_{24}CrN_3O_6S_3$	56.08		13.61
VI	$Rh(acacSCN)_3$	90	208–212[b]			16.92	$C_{18}H_{18}N_3O_6RhS_3$	37.83		16.83
VII	$Cr(dbmSCN)_3$	50	245–247[c]			10.87	$C_{48}H_{30}CrN_3O_6S_3$	64.56		10.77
VIII	$Co(dbmSCN)_3$	13	152–160[d]			10.59	$C_{48}H_{30}CoN_3O_6S_3$	64.06		10.69
IX	$Cr(dbmH)(dbmSCN)_2$	14	229–231	67.80		7.84	$C_{47}H_{31}CrN_2O_6S_2$	67.53		7.67
X	$Co(dbmH)(dbmSCN)_2$	3.5					$C_{47}H_{31}CoN_2O_6S_2$	66.98		7.61
XII	$Rh[acacSP(O)(OEt)_2]_3$	60		36.23	9.87	10.60	$C_{27}H_{48}O_{15}P_3RhS_3$	35.85	10.27	10.63
XIII	$Cr[bzacSP(O)(OEt)_2]_3$	25		48.73	8.74	9.01	$C_{42}H_{54}CrO_{15}P_3S_3$	48.51	8.93	9.25
XIV	$Cr[bzacSP(O)(OEt)_2]_3$	8.5		48.38	9.08	9.22	$C_{42}H_{54}CrO_{15}P_3S_3$	48.51	8.93	9.25
XVI	$Cr[dbmSP(O)(OEt)_2]_3$[e]	68	199–203	55.74	7.72	7.59	$C_{57}H_{60}CrO_{15}P_3S_3$	55.83	7.58	7.85
XVII	$Cr(dbmH)[dbmSP(O)(OEt)_2]_2$[e]	17	125–135	60.16	5.44	6.17	$C_{53}H_{51}CrO_{12}P_2S_2$	60.16	5.85	6.06
XVIII	$Cr(dbmH)_2[dbmSP(O)(OEt)_2]$[e]	1				3.22	$C_{49}H_{42}CrO_9PS$	66.13	3.48	3.60
XVI	$Cr[dbmSP(O)(OEt)_2]_3$[f]	30	199–203	55.72	7.38	7.85	$C_{57}H_{60}CrO_{15}P_3S_3$	55.83	7.58	7.85
XVII	$Cr(dbmH)[dbmSP(O)(OEt)_2]_2$[f]	8	124–133		5.60	6.01	$C_{53}H_{51}CrO_{12}P_2S_2$	60.16	5.85	6.06
XVIII	$Cr(dbmH)_2[dbmSP(O)(OEt)_2]$[f]	0.3					$C_{49}H_{42}CrO_9PS$	66.13	3.48	3.60
XIX	$\{Cr[dbmSP(O)(OEt)_2]_2(dbmS)\}_2$[f]	15	141–148	58.53	5.58	8.61	$C_{106}H_{100}Cr_2O_{24}P_4S_6$	58.45	5.69	8.83
XX	$Co[dbmSP(O)(OEt)_2]_3$	48		55.88		7.88	$C_{57}H_{60}CoO_{15}P_3S_3$	55.52	7.54	7.80
XXI	$Co(dbmH)[dbmSP(O)(OEt)_2]_2$	7					$C_{53}H_{51}CoO_{12}P_2S_2$	59.77	5.82	6.02
XXIII	$Cr(bzacSC_2H_4Cl)_3$	73.5	152–156[g]		(12.51)	11.68	$C_{36}H_{36}Cl_3CrO_6S_3$	52.78	(12.98)	11.74
XXIV	$Rh(acacSC_2H_4Cl)_3$	62	166–171[g]	37.85	(14.56)	13.40	$C_{21}H_{30}Cl_3O_6RhS_3$	36.88	(15.55)	14.07
XXV	$Cr(dbmSC_2H_4Cl)_3$	82		61.15	(10.41)	9.38	$C_{51}H_{42}Cl_3CrO_6S_3$	60.92	(10.58)	9.57
XXVI	$Co(dbmSC_2H_4Cl)_3$	30			(10.21)	9.22	$C_{51}H_{42}Cl_3CoO_6S_3$	60.51	(10.51)	9.50
XXVII	$Ru(acacSC_2H_4Cl)_3$	51	154–156[g]	39.27	(13.81)	39.27	$C_{21}H_{30}Cl_3O_6RuS_3$	36.98	(15.59)	14.10

[a] mp 172–173°C [11]. [b] Recrystallized from alcohol; mp 214–215°C [10]. [c] mp 230–231°C [11]. [d] mp 194–195°C [11]. [e] Product of reaction with triethylphosphite. [f] Product of reaction with potassium diethylphosphite. [g] After recrystallization from benzene-heptane mixture.

The mixture with general composition of $Cr(dbmH)_x\cdot(dbmSCN)_{3-x}$ was obtained by treatment of $Cr(dbmH)_3$ with half of equivalent of thiocyanogen. TLC of the mixture revealed four products: the upper and the bottom chromatographic zones were assigned to $Cr(dbmH)_3$ and trisubstituted chelate **VII**, whereas the two middle zones contained dibenzoylmethenates with one and two thiocyanate groups. Increasing the amount of thiocyanogen introduced into the reaction led to sequential elimination of the upper chromatographic zones, proving that the chromatographic mobility of thiocyanate derivatives of chromium dibenzoylmethenate decreased with more of thiocyanate groups. The ratio of **VII** and **IX** was of approximately 3.5 : 1.

Table 2. Selected IR spectra parameters (ν, cm^{-1}) of compounds **III–XXVII**

Comp. no.	SCN	Ph	(C=O, chel.)	Chelate ring	P–O–C, P–S–C, P=O
V	2150	1580	1533	1428, 1365, 1336	
VI	2150		1550	1413, 1366, 1335, 1060, 1031	
VII	2150	1598, 1582	1517	1444, 1420, 1339, 1307, 749, 701	
IX	2149	1597, 1583	1521, 1479	1444, 1422, 1342, 1304, 746, 701	
XII			1545	1415, 1361, 1332	1255, 1241, 1040 1017, 968
XIII		1580	1539	1427, 1342	1252, 1018, 969
XVI		1598, 1581	1518	1444, 1415, 1335, 1307	1258, 1248, 1014, 970
XVII		1596, 1583	1523, 1480	1444, 1414,1371, 1337	1251, 1017, 970
XIX		1599, 1581	1516	1444, 1413, 1334, 1304	1254, 1018, 970
XX		1598, 1581	1518	1444, 1415, 1333	1258, 1248, 1014, 970
XXIII		1579	1533	1410, 1337, 734, 704	
XXIV			1539	1411, 1358, 1329, 1063, 1022	
XXV		1598, 1581	1512	1445, 1407, 1332, 1304, 746, 702	
XXVII			1520	1406, 1355, 1330, 1259, 1059	

The yield of cobalt complexes in reaction (1) was about three times lower than in the cases of chromium complexes, likely due to intramolecular redox reactions typical of Co(III) complexes. The ratio of the tri- and disubstituted chelates was similar to that in the case of chromium complexes. Due to the low yield, the $Co(dbmH)(dbmSCN)_2$ complex X was not studied in detail; its structure was confirmed by TLC [R_f was identical to that of $Co(dbmH)(dbmSCN)_2$ in the $Co(dbmH)_x(dbmSCN)_{3-x}$ model mixture]. Furthermore, the chromatographic mobility of **X** was identical to that of disubstituted chromium dibenzoylmethenate **IX**. In our experience with a variety of chromium(III), cobalt(III) and rhodium(III) β-diketonates, in the case of octahedral complexes with the same ligands, the chromatographic mobility was virtually independent on the complex forming ion.

The new SCl-substituted diketonates were further used to prepare previously unknown thiophosphate complexes via the reaction described for the case of $Cr[acacSP(O)(OEt)_2]_3$ [1].

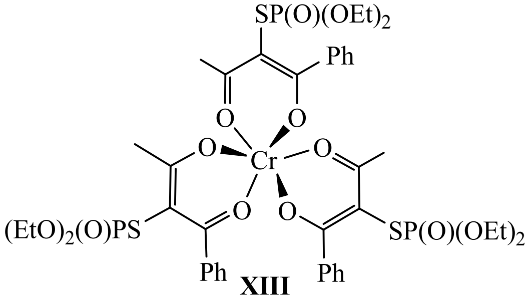
Treatment of chelates **I** and **II** with diethylphosphoric acid led to trisubstituted thiophosphates.

$$\underset{\mathbf{I,\ II}}{M(dikSCl)_3} + HP(O)(OEt)_2 \rightarrow \underset{\mathbf{XI,\ XII}}{M[dikSP(O)(OEt)_2]_3}, \quad (2)$$

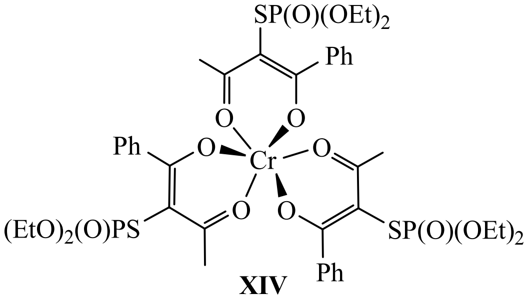
M = Cr, dik = bzac (**I, XI**); M = Rh, dik = acac (**II, XII**).

The rhodium complex **XII** was obtained with yield of 60%. Similarly to $Cr[acacSP(O)(OEt)_2]_3$ [1], **XII** was isolated in the form of viscous mass, crystallizing within 2–3 months of incubation. Due to excellent solubility in organic solvents, the product could not be recrystallized. In the IR spectrum of **XII**, the bands of thiophosphate group were observed along with the common bands of substituted acetylacetonate (Table 2). Besides thiophosphate **XII**, some minor products were revealed in the reaction mixture by TLC (not studied).

In the reaction of benzoylacetonate **I** with $HP(O)(OEt)_2$ two major products were obtained (yields of 25% and 8.5%). According to elemental analysis, the both products were trisubstituted thiophosphates $Cr[bzacSP(O)(OEt)_2]_3$ (Table 1). Due to outstanding adsorption of thiophosphate group, upon chromatographic isolation the product was separated into *trans*(*mer*) **XIII** and *cis*(*fac*) **XIV** isomers.



XIII



XIV

We did not attempt to experimentally elucidate the stereo configuration of the isomers: NMR is commonly used to do that, but the study was impossible in the case of paramagnetic chromium complexes. However, from the statistical point of view, the *trans* isomer should prevail, at *trans*/*cis* ratio of 3 : 1. As the ratio of the isolated products was close to 3 : 1, likely, **XIII** was the *trans* isomer. Moreover, that product was chromatographically more mobile, was in accordance with the literature data on higher mobility of *trans* octahedral complexes [7].

The above-given yields of **XIII** and **XIV** were significantly underestimated, due to partial destruction of the products in the course of chromatographic separation. Other substances formed in Eq. (2) could not be isolated in the pure form and, thus, were not studied.

An attempt to prepare the thiophosphate derivative of chromium dibenzoylmethenate via reaction (2) failed. Treatment of sulfenyl chloride **III** with one equivalent of diethylphosphoric acid led to a complex mixture of products containing $Cr(dbmH)_3$ and the compounds bearing one, two, or three thiophosphate groups. With two-fold excess of the acid, the sulfenyl chloride was completely transformed into unsubstituted chelate [Eq. (3)].

$$Cr(dbmSCl)_3 + 6HP(O)(OEt)_2 \rightarrow Cr(dbmH)_3. \quad (3)$$

Such processes were described in detail in the study of substitution reactions of metal halogenoacetylacetonates [Eqs. (4), (5)] [8].

$$Cr_{1/3}(acacBr) + HSEt \rightarrow Cr_{1/3}(acacSEt) + HBr, \quad (4)$$

$$Cr_{1/3}(acacSEt) + HSEt \rightarrow Cr_{1/3}(acacH) + EtSSEt. \quad (5)$$

We proposed that the similar processes occurred during the interaction of **III** with diethylphosphoric acid [Eqs. (6), (7)].

$$Cr_{1/3}(dbmSCl) + HP(O)(OEt)_2 \rightarrow Cr_{1/3}[dbmSP(O)(OEt)_2], \quad (6)$$

$$Cr_{1/3}[dbmSP(O)(OEt)_2] + HP(O)(OEt)_2 \rightarrow Cr_{1/3}(dbmH). \quad (7)$$

Reactions (6) and (7) occurred simultaneously, therefore, with less than two phosphite molecules with respect to SCl group a mixture of $Cr(dbmH)_3$ with the complexes containing one, two, or three thiophosphate groups was formed, its components being observed by TLC. Furthermore, the mixture should have contained the complexes with unreacted SCl groups. Those complexes were observed as the starting spots: SCl groups were irreversibly bound to the sorbent silanol groups and thus could not move along the plate.

As shown in [8], presence of hydrogen ions was the necessary condition for thio substituent to be eliminated Eq. (5). Evidently, in the studied case that was fulfilled due to release of hydrogen chloride upon Cl atoms substitution with phosphonate group [Eq. (6)].

Noteworthily, the substituents elimination was not observed in the reaction of $Cr(acacSCl)_3$ **XV** with diethylphosphoric acid [1]. However, after prolonged treatment of **XV** with excess of acidic phosphite, we observed the formation of mixture of partially substituted thiophosphates $Cr(acacH)_x[acacSP(O)(OEt)_2]_{3-x}$ (general formula). Similar result was achieved upon treatment of the individual $Cr[acacSP(O)(OEt)_2]_3$ complex with diethylphosphoric acid in the presence of hydrogen chloride. Thiols could be used instead of diethylphosphoric acid [Eq. (8)].

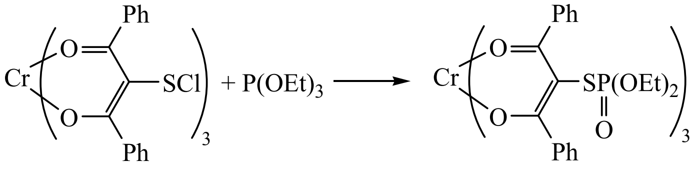
$$Cr[acacSP(O)(OEt)_2]_3 + 3HSPh \xrightarrow{HCl} Cr(acacH)_3. \quad (8)$$

Vice versa, thioalkyl groups bound to the metal chelate cycle could be removed by diethylphosphoric acid [Eq. (9)].

$$Cr(dbmSCH_2CH_2Cl)_3 + 3HP(O)(OEt)_2 \xrightarrow{HCl} Cr(dbmH)_3. \quad (9)$$

Thus, the discovered reaction of thiophosphate group elimination and the previously described elimination of thioalkyl and thioaryl substituents were examples of the general case of elimination of the groups bound to metal chelate ring via sulfur atom; thiols and secondary phosphites could be used in the reaction. In fact, the reaction was of reduction type, and other reducers could probably act similarly. In the case of dibenzoylmethenate complexes, the reaction was facilitated as compared to the metal acetylacetonates. The difference in reactivity could be due to steric repulsion of the two bulky β-substituents (phenyls) and the thio substituent bound to the central carbon atom of the chelate cycle in the case of dibenzoylmethenates. If so, the elimination of γ-substituent weakening the repulsive interactions should be favorable.

In order to avoid the substituent elimination, we performed the substitution in the neutral medium, with triethylphosphite as phosphorylating agent. Using triethylphosphite to prepare $Cr[acacSP(O)(OEt)_2]_3$ was described in [5].



III **XVI** (10)

The major product of the interaction between sulfenyl chloride **III** with triethylphosphite was the $Cr[dbmSP(O)(OEt)_2]_3$ complex (yield 68%).

Besides the major product, the complexes $Cr(dbmH)[dbmSP(O)(OEt)_2]_2$ (**XVII**) and $Cr(dbmH)_2[dbmSP(O)(OEt)_2]$ (**XVIII**) were isolated and identified (yields of 17% and 1%, respectively). Moreover, $Cr(dbmH)_3$ was found in trace amount (TLC). The mentioned products ratio was not constant, but varied from run to run. It was a function of the reagents mixing rate, reaction temperature, and other factors. Dropwise addition of triethylphosphite increased the yield of reduction products.

Another reaction tested as route to prepare thiophosphates from the sulfenyl chlorides was interaction with phosphite metal salt. We suggested that performing the reaction under basic conditions could completely prevent the γ-substituent elimination. In the reaction of **III** with potassium diethylphosphite, formation of tri-, di-, and monosubstituted products (yields 30%, 8%, and 0.3%, respectively) was observed. Additionally, another complex was isolated, less chromatographically mobile than the trithiophosphate-substituted chelate. The analysis of that product revealed two tris(dibenzoylmethenate) groups bound via disulfide bridge in its structure.

$$\underset{\textbf{III}}{2Cr(dbmSCl)_3} + 6KP(O)(OEt)_2$$

$$\rightarrow \underset{\textbf{XIX}}{[(EtO)_2P(O)Sdbm)_2Cr(dbmS\text{-})]_2}. \qquad (11)$$

The dimer **XIX** yield was of 15%. One more product was found in the mixture, with even lower chromatographic mobility. Due to its low yield, the latter product was not isolated; we suggest it was a trimer.

The total yield of monomeric phosphorylated diketonates was decreased to 38% (30 + 8 + 0.3) with potassium diethylphosphite as compared to 86% (68 + 17 + 1) with triethylphosphite; that was in line with results reported in [3]: using of hard nucleophile decreased the target products yield due to destruction of the diketonate cycle as well as due to symmetrization (combination of thiodiketonate groups to form polymers) reaction. Such products were described as oligomers mixture in [3], none of them was isolated. Therefore, complex **XIX** was the first individual characterized product of symmetrization reaction.

The $Co[dbmSP(O)(OEt)_2]_3$ (**XX**) complex was obtained with 48% yield in the reaction of **IV** with triethylphosphite. Moreover, disubstituted chelate $Co(dbmH)[dbmSP(O)(OEt)_2]_2$ (**XXI**) was obtained with 7% yield; it was identified by TLC as compared with the disubstituted chromium complex **XVII**. Similarly to other examples, the total yield of the products was lower than in the case of chromium complexes.

The reaction with ethylene gave β-chlorosulfide derivatives [Eq. (12)].

$$\underset{\textbf{I, II, III, IV, XXII}}{M(dikSCl)_3} + 3CH_2{=}CH_2 \rightarrow \underset{\textbf{XXIII–XXVII}}{M(dikSCH_2CH_2Cl)_3}, \qquad (12)$$

M, dik = Cr, bzac (**I**, **XXIII**); Rh, acac (**II**, **XXIV**); Cr, dbm (**III, XXV**); Co, dbm (**IV, XXVI**); Ru, acac (**XXII, XXVII**).

In the reaction (12), highest yield of products with elemental analysis coinciding with the calculated values was achieved in the cases of chromium, rhodium, and ruthenium complexes. The structure of **XXIV** was additionally confirmed by NMR spectroscopy, those of **XXIV** and **XXVII** were confirmed by MS studies. Besides the molecular ions corresponding to $M(acacSC_2H_4Cl)_3$, the signals assigned to the processes of sequential elimination of SC_2H_4Cl- and $acacSC_2H_4Cl$- were identified (Table 3). The isotopic compositions of the ions coincided with the calculated values (Isotopes Calculator from NIST software package).

The cobalt complex **XXVI** was obtained with moderate yield, likely, due to losses during the chromatographic purification. After **XXVI** had passed through the column, silica gel was pink, the color was typical of Co(II) complexes. During several months storage, **XXVI** partially decomposed as well. In the case of thiophosphate-substituted cobalt dibenzoylmethenate **XX** the decomposition was not observed, and the complex was stable over several years of storage. We suppose that the lower stability of **XXVI** was due to increase of the electron density in the chelate ring by SC_2H_4Cl group, thus favoring the intramolecular redox reaction of Co^{+3}. The electron-accepting effect of the $SP(O)(OEt)_2$ group decreased the electron density in the chelate cycle, thus stabilizing the complex **XX**.

The purity of SCH_2CH_2Cl-substituted acetylacetonate and benzoylacetonate complexes (**XXIII**, **XXIV**, and **XXVII**) was confirmed by TLC: introduction of SCH_2CH_2Cl into acetylacetonate complex significantly decreased the chelate adsorption and thus the complexes were more mobile. That allowed easy separation of the complexes with different number of substituents. The purity of dibenzoylmethenate complexes **XXV** and **XXVI** could not be checked by TLC, as non-substituted complexes and SCH_2CH_2Cl-substituted ones revealed similar chromatographic parameters.

It is known that in the IR spectra of non-substituted β-diketonates two intense bands are to be found in the range of 1600–1500 cm^{-1}, assigned to C=O and C=C vibrations. In the spectra of substituted complexes, both the bands fused into a single one [9]. In the spectra of partially substituted acetylacetonates, the pair of bands of the non-substituted cycles overlapped with the single band of the substitutes rings [6]. In IR spectra of partially substituted dibenzoylmethenates **IX** and **XVII** only a single intense band was observed at 1600–1500 cm^{-1}. The observed effect was because the two bands of C=O and C=C vibrations of non-substituted dibenzoylmethenates were close and partially overlapped. The additional overlap with the single band of the substituted cycle gave a common band.

The band of medium intensity at 1591 cm^{-1} in the spectrum of $Cr(dbmH)_3$, assigned to phenyl fragments vibrations [9], was split into two bands of lower intensity (1597 and 1581 cm^{-1}) in the cases of substituted complexes. In the spectra of non-substituted dibenzoylmethenates, a strong band was observed at 1479 cm^{-1}, not assigned. In the spectra of partially substituted complexes (**XVII** and **XVIII**), that band was weaker and completely vanished in the cases of fully substituted chelates.

To conclude, the reported study showed that sulfenyl chloride derivatives of rhodium and ruthenium acetylacetonates as well as of β-phenyl-containing chromium and cobalt diketonates, could participate in the reactions typical of chromium, cobalt, and aluminum acetylacetonates. However, in all the cases a number of side products were formed; that was especially so in the cases of dibenzoylmethenate complexes – in the latter case, sulfur-containing substituents were easily eliminated, contaminating the products with partially substituted complexes. Therefore, reactions of sulfenyl derivatives of dibenzoylmethenates should be performed under conditions preventing the free acid formation.

Table 3. Mass spectra parameters of **XXIV** and **XXVII**

Ion	XXIV		XXVII	
	m/*z*	*I*, %	*m*/*z*	*I*, %
$[M(acacSC_2H_4Cl)_3]^+$	682	4	680	22
$[M(acacSC_2H_4Cl)_3\text{-}1]^+$	681	3		
$[M(acacSC_2H_4Cl)_3\text{-}2]^+$	680	5		
$[M(acacSC_2H_4Cl)_2(acacCl)]^+$	622	10	620	14
$[M(acacSC_2H_4Cl)_2(acac)]^+$			585	
$[M(acacSC_2H_4Cl)(acacCl)_2]^+$	562	4	560	15
$[M(acacSC_2H_4Cl)_2Cl]^+$			525	4
$[M(acacSC_2H_4Cl)_2]^+$	489	8		
$[M(acacSC_2H_4Cl)(acacCl)]^+$	429	23		

EXPERIMENTAL

IR spectra at 4000–400 cm^{-1} were recorded with Impact 400 (Nicolet) spectrometer, in KBr pellets. ^1H NMR spectra were registered with Bruker WM-250 spectrometer at 250 MHz in $CDCl_3$ with TMS as reference. Mass spectra were registered with LKB-9000 unit (direct injection, ionizing voltage of 70 eV). TLC analysis was performed with Sorbfil PTSKh-A-UF plates, with benzene or benzene–acetone (10 : 1) as mobile phase. The chromatographic zones were detected according to the spots coloration in natural light and in UV (254 nm). Silica gel LaChema (100–160) was used for chromatographic purification.

Sulfenyl chlorides **I, III**, and **IV** were prepared in THF as described in [6]. Sulfenyl chlorides **II** and **XXI** were prepared in hexane [6]. All sulfenyl chlorides (except for **III**) were prepared straight before using and were not purified. Yields and basic analytical characteristics of the prepared substances are collected in Table 1, spectral data are given in Tables 2 and 3.

The model mixtures of thiocyanates M(dbmH)$_x$·(dbmSCN)$_{3–x}$ (M = Cr, Co) were prepared as described in [11], by adding the calculated amount of thiocyanogen [solution in chloroform, Pb(SCN)$_2$: Br$_2$ = 1 : 1, metal : thiocyanogen = 1 : 2] to a solution of unsubstituted chelate (0.2 g) in chloroform (6 mL). The reaction mixture was stirred during 2 h, washed with water, dried over MgSO$_4$ and applied to chromatography test without further purification. In benzene, R_f were as follows: Cr(dbmSCN)$_3$ – 0.27, Cr(dbmH)·(dbmSCN)$_2$ – 0.36, Cr(dbmH)$_2$(dbmSCN) – 0.47, and Cr(dbmH)$_3$ – 0.68. The corresponding cobalt complexes revealed the same values of R_f.

Tris(2-thiocyano-1-phenylbutane-1,3-dionato)-chromium(III) (V). 30 mmol of KCN in 25 mL of glacial acetic acid was added in a single portion to solution of 5 mmol of Cr(bzacSCl)$_3$ in 25 mL of THF upon stirring. After 0.5 h, the mixture was poured into water and extracted with chloroform. After drying over MgSO$_4$, the solvent was evaporated under vacuum at 40–50°C, and the product was isolated by chromatography with benzene as eluent.

Tris(3-thiocyanopentane-2,4-dionato)rhodium(III) (VI) was prepared similarly. The product was isolated by chromatography with benzene–acetone as eluent, with stepwise increase of acetone fraction [(10 : 0) to (10 : 1)].

Interaction of Cr(dbmSCl)$_3$ with potassium cyanide was performed similarly. The products **VII** and **IX** were isolated by chromatography with benzene as eluent. R_f 0.27 (**VII**) and 0.36 (**IX**).

Interaction of Co(dbmSCl)$_3$ with potassium cyanide was performed similarly.

Tris(3-S-diethylthiophosphatopentane-2,4-dionato)rhodium(III) (XII). A cooled solution of HPO(OEt)$_2$ (20 mmol) in 10 mL of chloroform was added upon stirring in a single portion to a cooled (0°C) solution of Rh(acacSCl)$_3$ (5 mmol) in 50 mL of chloroform. After 15 minutes the reaction mixture was washed with water and dried over MgSO$_4$. The solvent was evaporated; the products were isolated from the residue by chromatography with benzene–acetone as eluent, with stepwise increase of acetone fraction [(100 : 1) to (100 : 10)].

Isomers of tris(3-S-diethylthiophosphate-1-phenylbutanedionato-1,3)chromium(III) (**XIII** and **XIV**) were prepared similarly.

Interaction of Cr(dbmSCl)$_3$ with excess of diethylphosphoric acid. A solution of HPO(OEt)$_2$ (2 mmol) in 2 mL of chloroform was added upon stirring in a single portion to a cooled (0°C) solution of Cr(dbmSCl)$_3$ (0.5 mol) in 10 mL of chloroform. After 15 min the reaction mixture was washed with water and dried over MgSO$_4$. The solvent was evaporated; the residue was recrystallized from benzene–hexane mixture. Cr(dbmH)$_3$ was obtained, R_f 0.68 (benzene), mp 312–316°C {reference data: R_f 0.68 (benzene), mp 317–318°C [9]}.

Interaction of Cr[acacSP(O)(OEt)$_2$]$_3$ with thiophenol. Dry hydrogen chloride was passed through solution of Cr[acacSP(O)(OEt)$_2$]$_3$ (1 mmol) and thiophenol (4 mmol) in 10 mL of chloroform at room temperature during 5 min. After 10 min the mixture was washed with water and dried over MgSO$_4$. The solvent was evaporated; the residue was washed with ethanol–hexane mixture and recrystallized from benzene–hexane. Cr(acacH)$_3$ was formed, R_f 0.56 (benzene–acetone, 10 : 1), mp 209–211°C (reference data: R_f 0.56, mp. 214°C.

Interaction of Cr[acacSP(O)(OEt)$_2$]$_3$ with diethylphosphoric acid was performed similarly. After 1 h, TLC revealed the major violet zone of [Cr(acacH)$_3$] and two minor violet zones, likely, of Cr(acacH)$_2$·[acacSP(O)(OEt)$_2$] and Cr(acacH)[acacSP(O)(OEt)$_2$]$_2$. The parent Cr[acacSP(O)(OEt)$_2$]$_3$ was present in the mixture in trace amount.

Interaction of Cr(dbmSCl)$_3$ with triethylphosphite. Solution of P(OEt)$_3$ (8 mmol) in 10 mL of THF was added dropwise under stirring to a cooled (–20°C) solution of Cr(dbmSCl)$_3$ (2 mmol) in 50 mL of THF. After 3 h, the reaction mixture was poured into water and extracted with chloroform. After evaporation of the solvent, the products were separated by chromatography with benzene–ethyl acetate as eluent, with stepwise increase of ethyl acetate fraction [(100 : 1) to (100 : 3)]. The products **XVI**, **XVII**, and **XVIII** were isolated.

Interaction of Co(dbmSCl)$_3$ with triethylphosphite was performed similarly; complexes **XX** and **XXI** were obtained.

Interaction of Cr(dbmSCl)$_3$ with potassium diethylphosphonate. Solution of potassium diethylphosphite: 25 mmol of HPO(OEt)$_2$ was added to the excess of fine cut metal potassium in 25 mL of THF; after spontaneous reaction, the solution was refluxed during 0.5 h. Title interaction: solution of KPO(OEt)$_2$ was added upon stirring to a cooled (–20°C) solution of

$Cr(dbmSCl)_3$ (4 mmol) in 100 mL of THF. After 0.5 h the mixture was poured into water and extracted with chloroform. The solvent was evaporated under vacuum, and the solid residue was separated by chromatography with benzene–ethyl acetate with stepwise increase of ethyl acetate fraction [(100 : 1) to (100 : 10)]. **XVI**, **XVII**, **XVIII**, and **XIX** were isolated.

Interaction of sulfenyl chlorides diketonate complexes with ethylene. Dry ethylene was passed through a solution of $M(dikSCl)_3$ (5 mmol) in 10 mL of chloroform. The reaction was monitored by TLC (benzene as eluent, till the starting spot disappeared). The solvent was evaporated, the solid residue was purified by silica gel chromatography with benzene as eluent.

^{1}H NMR spectrum of $Rh(acacSCH_2CH_2Cl)_3$, δ, ppm: 2.62 s (6H, $2CH_3$), 2.82 d. t (2H, SCH_2, *J* 3.5, 9 Hz), 3.59 d. t (2H, CH_2Cl, *J* 3.5, 9 Hz).

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